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IITRI

Contract No. SNPC-66
IITRI Project No. G6029
Final Report

METAL CARBIDE-GRAPHITE COMPOSITES STUDIES

Prepared for

Space Nuclear Propulsion Office
Cleveland Extension
NASA
21000 Brookpark Road
Cleveland, Ohio 44135
Attention: Mr. J. J. Lombardo

IIT RESEARCH INSTITUTE

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616

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ABSTRACT

The objective of this phase of a research program directed toward improving the high temperature mechanical properties of metal carbide-graphite composites, was to lower fabrication temperatures and still retain these desirable properties. Previous experiments indicated that in order to obtain good high temperature mechanical properties, hot-pressing required temperatures close to the carbide-carbon eutectic temperature. For the composites under consideration, NbC-C and TaC-C, the fabrication temperatures required were in the 3150-3200°C temperature range.

Previous experiments indicated that the additions of a low melting refractory metal carbide produced better graphite in the composite structure and would form a highly refractory solid solution. Both of these phenomena will produce a stronger, more creep resistant structure. While these reactions take place at a lower temperature than the normal hot-pressing temperature the resultant structure, from phase diagram analysis, should retain its refractory characteristics to temperatures approaching 3150°C. NbC-C and TaC-C composites were hot-pressed with addition of up to 50% W at temperatures of 3000°C. The results of these experiments were compared to standard NbC-C composites fabricated at 3150°C and 3000°C. The data from these experiments revealed that the W containing composites fabricated at 3000°C possessed superior mechanical properties when compared to NbC-C composites fabricated at temperatures of 3150°C and 3000°C.

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METAL CARBIDE-GRAPHITE COMPOSITES STUDIES

I. INTRODUCTION

With the increasing temperature requirements upon materials, metal carbide-graphite composites which have excellent high temperature properties are finding widespread use. Fabrication of NbC-C and TaC-C composites are normally conducted at 3150-3250°C, the temperature required to obtain maximum bonding.

The purpose of the present studies was to obtain carbide-graphite composites which exhibit good high temperature properties, under a more easily obtainable hot-pressing temperature of 3000°C or under. This involved the use of WC as an aid to improve densification and graphitization, and to subsequently form $NbC\text{-}WC_{(1-x)}$ solid solutions which would be deformation resistant.

Some interesting results of previous work at IITRI[1,2] have suggested that fabrication temperatures might be lowered to about 3000°C or less without sacrifice in composite properties. It has been established that amounts as small as 12 vol% of WC yielded strong (15,000 psi) composites with dense graphite matrices. This was accomplished at the relatively low fabrication temperature of 2800°C and can be attributed to exsolution of a dense graphite from the molten carbides on cooling. Furthermore, the earlier work indicated that deformation resistance of solid solutions of carbides was superior to that for either of the parent carbides. It was postulated that this was caused by the blocking of dislocation movement by the "impurity" carbide.

The use of boron carbide as an aid to lower fabrication temperature has also been considered. It has been reported that boron doping increases the high temperature strength of TiC[3] and $VC_{0.85}$[4] through the development of second-phase inclusions. Niobium carbide has an fcc structure as does TiC, and could develop a similar structure to produce a composite with higher high

temperature strengths. Furthermore, the boron (carbide) was expected to function as a graphitization aid due to its solubility in carbon.

The studies for this period have considered the following systems: NbC-WC-C, TaC-WC-C, and NbC-B_4C-C. Evaluations have included room temperature characterization of density, microstructure, lattice parameters, and flexural strength. High temperature investigations of flexural strength and thermal expansion behavior have been conducted. The most significant developments from our studies can be summarized as follows:

1. The NbC-WC-C composites fabricated at 3000°C exhibit properties which are equivalent, or superior to those for present state-of-the-art NbC-C composites. At the higher carbide levels, there is a marked superiority for tungsten carbide containing bodies.

2. Composites in which considerable liquification has occurred (as indicated by material loss) appear to exhibit higher strengths than those in which such material loss has not occurred. This is probably due to a solution-recrystallization process, and processing modifications to control material loss can probably produce the strongest composites possible.

3. The incorporation of WC in TaC-C composites fabricated at 3000°C results in material with excellent high temperature properties. These bodies display strengths at temperatures up to 2500°C, which are superior to those for TaC-C bodies hot-pressed at above 3200°C.

4. Preliminary work with B_4C as a fabrication aid for NbC-C composites suggests that high temperature strength is deleteriously affected. However, the very high densities and some high room temperature strengths suggest further study to determine the source of these data.

II. THEORETICAL CONSIDERATIONS

The mechanisms through which W acts as a fabrication aid may be explained with the help of the W-C phase diagram (Figure 1). As the NbC-C-W powder mixture is heated during hot-pressing, W reacts with C until the system is essentially NbC-C-WC at 2000°C. This has been shown by x-ray analysis. As a temperature of 2776°C is approached, increasing plasticity of WC probably aids in densification of the system. At about 2776°C, the WC undergoes a peritectic reaction to form a liquid having a composition of 42 atomic % W, and to precipitate solid carbon (graphite). With the formation of liquid, the lubrication action will cause particle rearrangement to occur under the influence of compressive forces to yield the most effective packing.

As the system is heated further, the composition of the liquid becomes richer in carbon as indicated by the liquidus on the phase diagram. In the liquid phase-aided reaction, less ordered graphite is dissolved in the liquid and precipitated as a more ordered phase, thus producing a more highly ordered graphite phase in the system.

The liquid will be a very mobile phase, especially under the pressures involved. A second reaction occurs when this tungsten-carbon liquid contacts niobium carbide. Solid solution is formed between NbC and a cubic $\propto$-$WC_{(1-x)}$ phase, precipitating out the excess graphite. The resultant solid solution is more refractory than WC; even at a fairly high $WC_{(1-x)}$ content of 30 mol%, the solidus is still about 3150°C (Figure 2).

Thus, the processes which occur during hot-pressing are: densification up to about 2800°C; further densification plus solution and recrystallization of graphite above 2800°C; and formation of a refractory NbC-$WC_{(1-x)}$ solid solution.

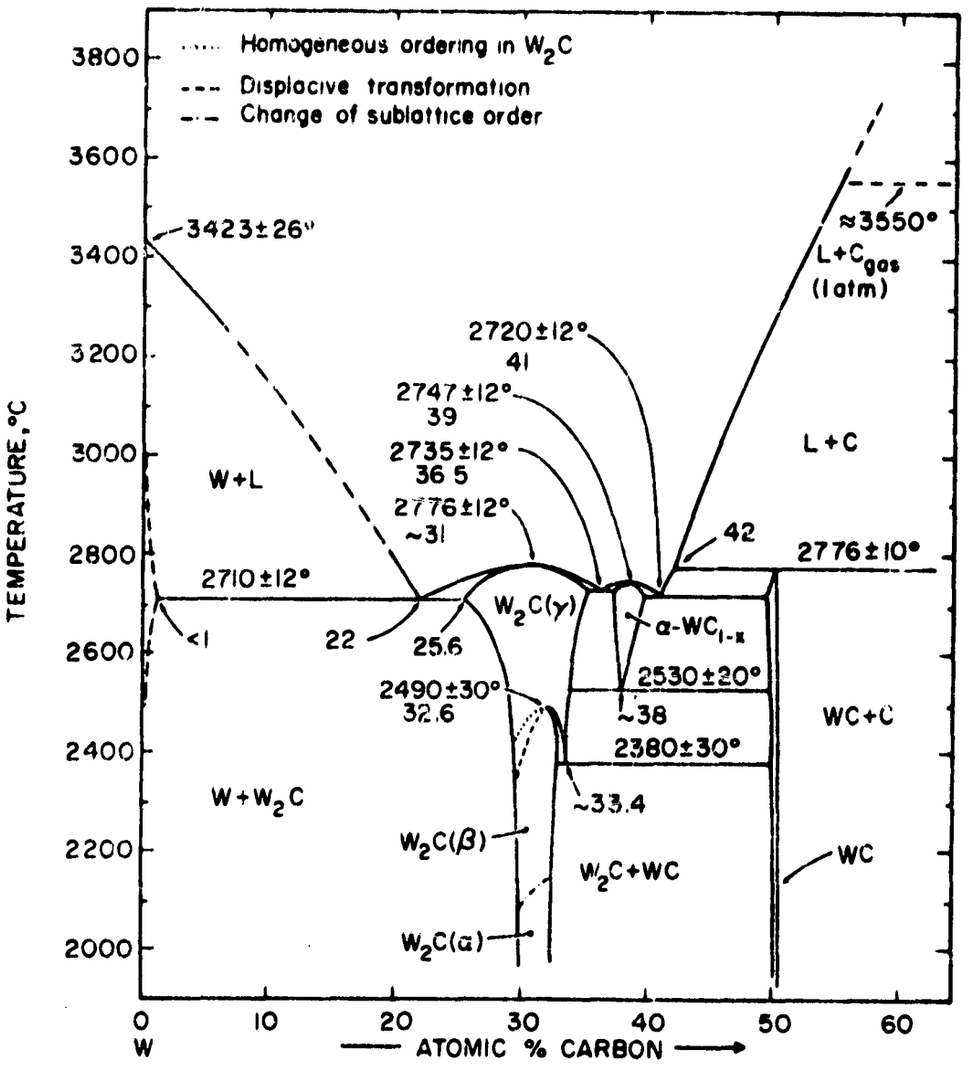


Fig. 1 TUNGSTEN-CARBON PHASE DIAGRAM
(Reference 5)

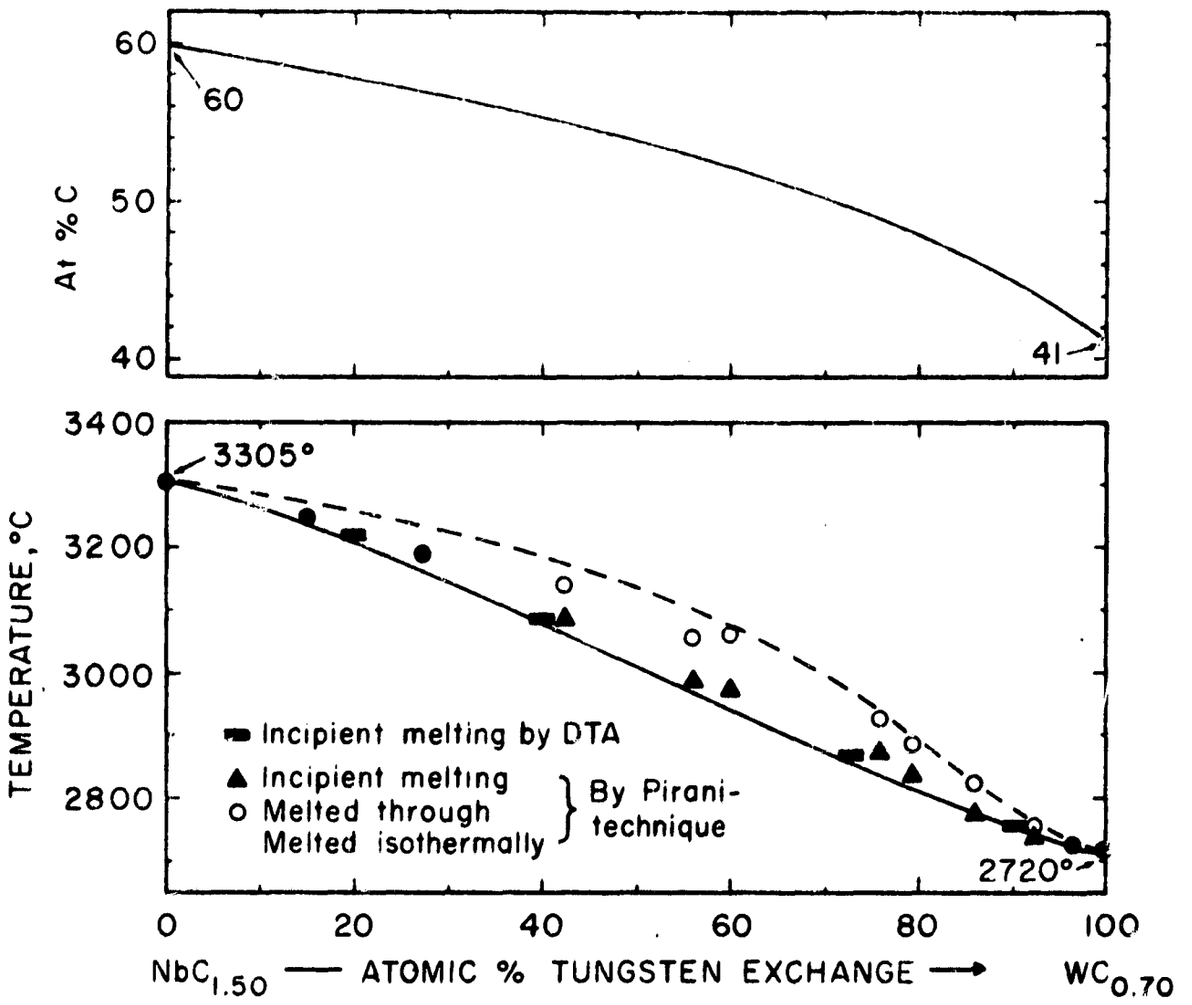


Fig. 2 MELTING ALONG THE $(NbC,W)C_{(1-x)}$+C EUTECTIC TROUGH (Reference 5)
TOP: METALLOGRAPHICALLY ESTIMATED COURSE OF THE EUTECTIC TROUGH

III. EXPERIMENTAL PROCEDURE

A. Preparation and Fabrication

The choice of starting powders and processing procedure used were based on information developed in past programs. This work had shown how composite properties could be controlled by varying carbide content, size, shape and purity of particles, and particle size relationships. The raw materials were restricted to a minimum number in order to minimize variables to be examined.

1. Raw Materials

The carbon powder used in our studies was M-3 graphite, a high purity material which is used by other laboratories such as Los Alamos Scientific Laboratory (LASL). The use of this powder facilitates comparison of data by elimination of raw material effect variables. Along with M-3 graphite, a portion of high purity niobium carbide (NbC-42A) was allotted to IITRI by LASL. This allowed correlation of mechanical properties with material fabricated at other laboratories. Tantalum carbide powder conforming to similar specifications as those for NbC, was obtained from Wah Chang; as shown in Table I, it is low in iron and is of a fine particle size.

The fabrication aids which were considered were tungsten and boron carbide. A very fine tungsten powder was obtained from Fansteel Inc. The small particle size was chosen in order to realize good dispersion of the W additive throughout the NbC-W-C mixture, and thus maximize the graphitization effect of WC during fabrication. An extremely fine B_4C also was evaluated. Again, the choice was dictated by the desire for extensive dispersion.

Descriptions of the various powders are given in Table I. The relative size and shape of the different particles are shown in the photomicrographs in Figure 3.

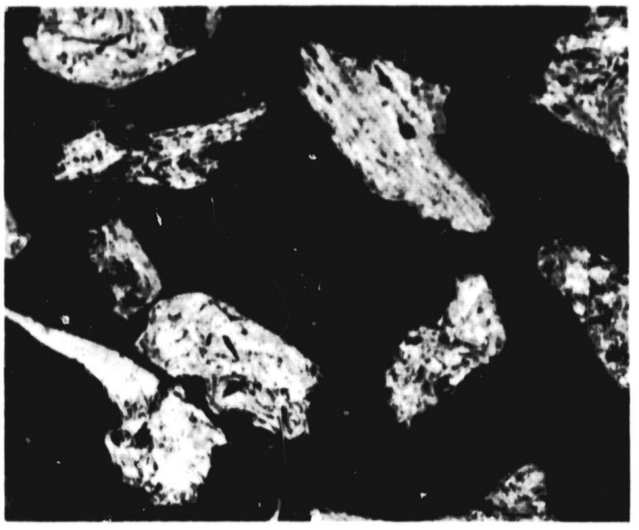
Table I

RAW MATERIALS USED FOR NbC-C AND NbC-WC-C COMPOSITES

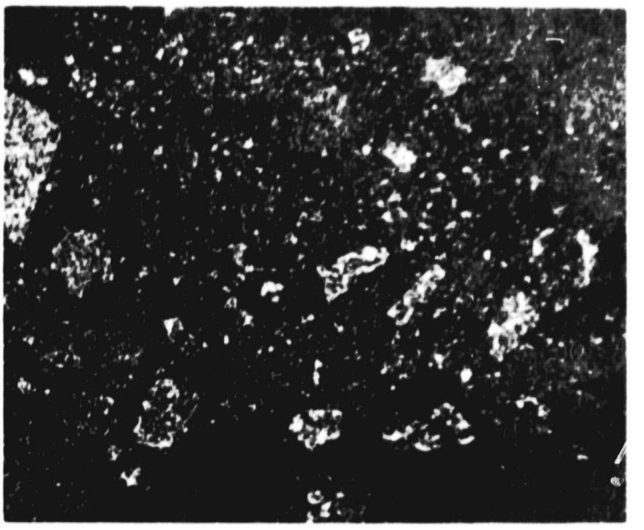
Material/Designation		Supplier	Particle Size	Chemical Analysis
Graphite	M3	Great Lakes Carbon (CMB-6:LASL)	44-105μ	Fe: 40 ppm O: 700 ppm
NbC	42A	Wah Change (CMB-6:LASL)	3.55μ*	Fe: 300 ppm O: 0.30%
TaC	SP11679A	Wah Change	2-3μ	Fe: 150 ppm
W	427-A	Fansteel	1.10μ*	Fe: 15 ppm O:1450 ppm
B_4C		Shieldalloy	< 500 mesh	N.D.

*Fisher Subsieve

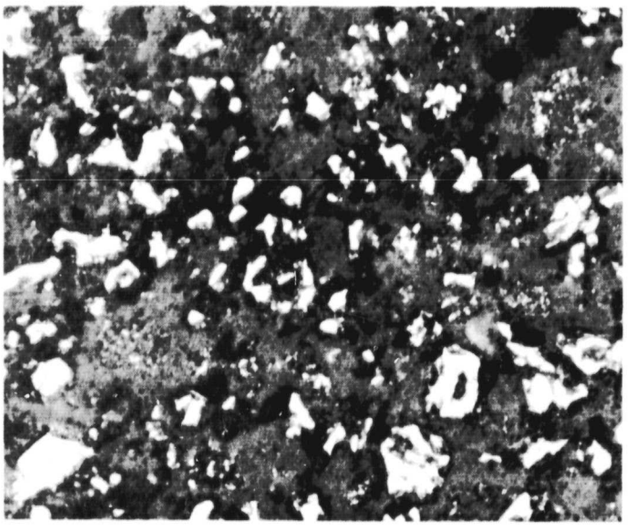
50 μ



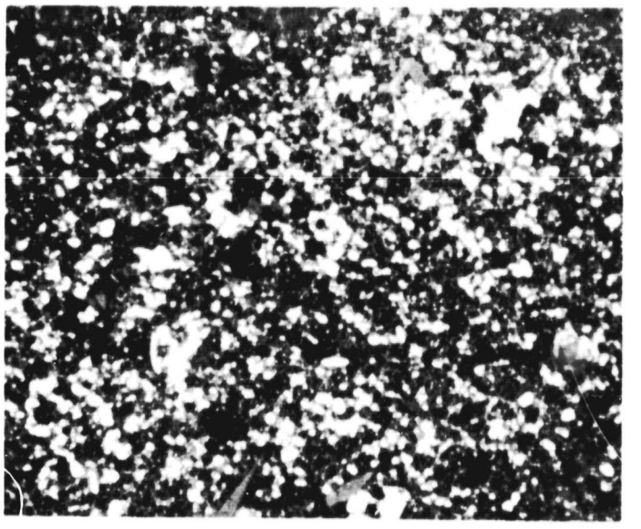
Neg. 36047
(a) M-3 Graphite Flour
44-105



Neg. 36051
(b) Tungsten, W-427A
1.10 (Fisher)



Neg. 37245
(c) Niobium Carbide, 42A
3.55 (Fisher)



Neg. 37246
(d) Tantalum Carbide, SP11679A
2-3

Mag. 200X

Fig. 3 PARTICLE SIZE AND SHAPE OF RAW MATERIALS FOR NbC-WC-C AND TaC-WC-C COMPOSITES

2. Processing Procedure

The various mixtures of NbC-C and NbC-W-C were blended by tumbling with rubber stoppers for 16 hrs. The use of rubber as opposed to ceramic or metal precludes any grinding action which could introduce undesirable impurities. This method has been found to provide good mixing of the particles of widely different densities, i.e., C - less than 2 g/cc, NbC - 7.8 g/cc, and W - 19.3 g/cc. Mixtures were then cold-pressed at 1000 psi prior to hot pressing.

The time-temperature-pressure schedules for the various pressings are shown in Figure 4. Schedule 1 involved temperatures of 3150-3200°C, the conditions required to obtain NbC-C composites with good bonding as established in earlier studies. Schedule 2 was the schedule of interest for composites incorporating tungsten as the densification aid. It had been shown in earlier work that 3000°C (Schedule 2) was too low a fabrication temperature to achieve good bonding in NbC-C composites.

B. Evaluation of Composites

Evaluation of composites included microstructural examination, x-ray analysis, microprobe analysis, and determination of physical mechanical, and electrical properties in both grain directions. The procedures are described in the following sections.

1. Room Temperature Evaluations

(a) Physical Properties

Initial evaluation of samples include determination of bulk density, microstructural examination, and analysis by x-ray and electron microprobe techniques. Measured bulk densities were compared to theoretical densities which were calculated based on x-ray densities of $NbC\text{-}WC_{(1-x)}$ solid solutions using the formula:

$$\rho = \frac{1.66020\ A}{V} \qquad (1)$$

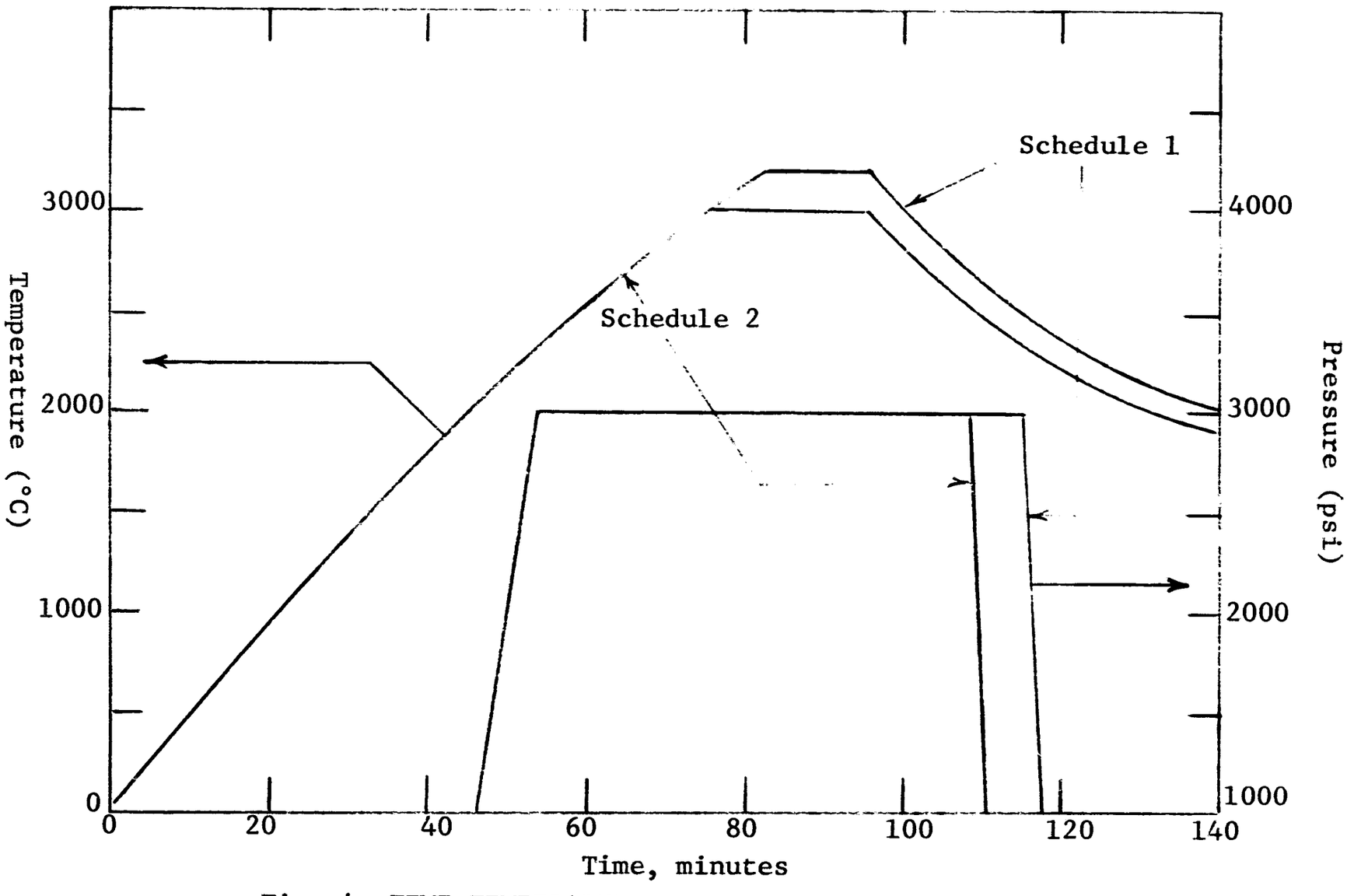


Fig. 4 TIME-TEMPERATURE-PRESSURE SCHEDULES FOR HOT PRESSING OF METAL CARBIDE-GRAPHITE COMPOSITES

where ΣA = sum of the atomic weights of the atoms in the unit cell, and V = volume of unit cell ($\AA^3$). For x-ray evaluations, Debye-Scherrer powder patterns were produced, and lattice parameters were determined from the films using the Nelson-Riley function. Microstructural examination was conducted on samples prepared using modified metallographic techniques. The use of a 30% H_2O_2 solution as a chemical polish-etch minimized smearing and pullouts.

The electron microprobe analyzer was employed to examine formation of solid solutions. This technique is based on the principle that when a metal is bombarded with high energy electrons, a portion of the kinetic energy is converted to x-radiation which contains components that are uniquely characteristic to the metal. The emitted radiation is analyzed by a spectrometer which can be tuned to a specific radiation, e.g., niobium. Grouped electron and x-ray image photographs are presented in this report. The former shows microstructure since the differing composition of the two phases possess differing reflectivities for the incident electron. The x-ray image is the result of tuning to a specific radiation which in our case is the particular metal carbide phase being studied.

(b) Mechanical Properties

Flexural strengths were determined using four-point loading, the load points being at the 1/3 points of 1-1/2 in. span. Sample dimensions were approximately 1/4 x 1/4 in. in cross section; lengths varied from 1-3/4 to 2-3/4 in. Room temperature measurements were conducted in an Instron testing machine. An extensometer was employed to record deflection of the sample; flexural modulus was determined from the x-y plot of stress vs strain. The use of flexural tests provide a rapid and simple screening of properties and trends. Thus, this type of evaluation was used to obtain the maximum amount of information about the various compositions studied in this phase.

Elevated temperature determinations of mechanical behavior were made in a graphite resistor tube furnace in an argon atmosphere. In flexural strength experiments, samples were heated to the respective test temperature in 5-8 min and soaked at this temperature for 10 min prior to testing. Load was monitored with a calibrated deflection ring.

(c) Thermal Expansion

The cathetometric method was used to determine thermal expansion behavior. Samples were taken through at least two cycles of room temperature to 2500°C in the graphite tube furnace.

(d) Compositional Designation

The compositions investigated during this program involve ternary as well as binary systems. In order to simplify compositional designations while retaining descriptiveness, the following scheme was used. For binary systems such as NbC-C, the designation consists of two numbers separated by a slash. For example, 25NbC/75M-3 refers to a 25 vol% NbC-75 vol% C composite prepared from NbC-42A and M-3 graphite (Table I). Ternary systems have three numbers; 20NbC/5WC/75M-3 contains 20 vol% NbC-42A, 5 vol% WC (added to the powder mixture as W metal), and 75 vol% M-3 graphite flour. It is understood that the NbC and WC form a solid solution, but this designation serves to describe what has gone into the composite.

IV. RESULTS AND DISCUSSION

The investigations for this report period were concerned with assessing the effect of using tungsten as a fabrication aid for both NbC-C and TaC-C composites. Preliminary experiments also were conducted with boron carbide as a fabrication aid. The results of these studies are detailed in the following sections.

A. Lattice Parameter Study

Experiments were conducted to determine lattice constants for $NbC\text{-}WC_{(1-x)}$ solid solutions and thus establish standards for x-ray analysis. Mixtures of NbC-W-C powders giving the final compositions

Mol% $WC_{(1-x)}$	Mol% NbC	Mol%C (Excess)
5	95	25
10	90	25
15	85	25
20	80	25
25	75	50
30	70	50
40	60	50
50	50	50

were mixed thoroughly with organic binder consisting of xylene and paraffin. The mixtures were dried in an oven at 70°C and pressed into pellets 3/4 in. in diameter and ~ 1/4 in. thick under a pressure of 10,000 psi. Firings were performed at 2800°C in a carbon tube furnace for 2 hrs under an argon atmosphere. Sintered pellets were ground, mixed with binder, pressed into pellets and fired again as before. Such processes were repeated 3 times for compositions 0-20 mol% NbC, and 4 times for compositions 25-50 mol% NbC, to obtain homogeneous $NbC\text{-}WC_{(1-x)}$ solid solutions.

X-ray diffractions using FeKα radiation were made on the solid solutions. Lattice parameters were calculated from

the back reflection lines using the Nelson-Riley graph. The final x-ray patterns showed only the lines of homogeneous $NbC\text{-}WC_{(1-x)}$ solid solution and graphite. No WC lines were detected. Apparently the NbC had dissolved all of the WC of the mixture, and a maximum amount of C into its lattice.

A comparison of our data with that of Rudy in Figure 5 shows reasonable agreement. Identification of solid solution composition by x-ray analysis utilized these data.

B. NbC-WC-C System

Studies of niobium carbide-graphite composites involved fabrication and evaluation of three sets of materials:

1. NbC-C composites fabricated at 3150-3200°C. These were to serve as state-of-the art standards to which the NbC-WC-C composites were compared.

2. NbC-C composites fabricated at 3000°C. These were fabricated at the same temperature as the NbC-WC-C composites so that the effect of WC would be the only variable.

3. NbC-WC-C composites. Compositional studies considered composites of about 15-75 vol% carbides in order to establish behavioral trends. The composition of the $NbC\text{-}WC_{(1-x)}$ solid solution was varied up to over 50 mol% $WC_{(1-x)}$. The bulk of the work was with materials of 10-20 mol% $WC_{(1-x)}$, the range which appeared most useful.

1. Physical Properties

(a) Density

Initial evaluation of all composites involved determination of density along with uniformity within a billet. The data for the various composites shown in Figure 6 reveal a trend of increasing values for % theoretical density with increasing carbide content. This is probably due to the fact that carbides are more easily densified than graphite which is difficult to

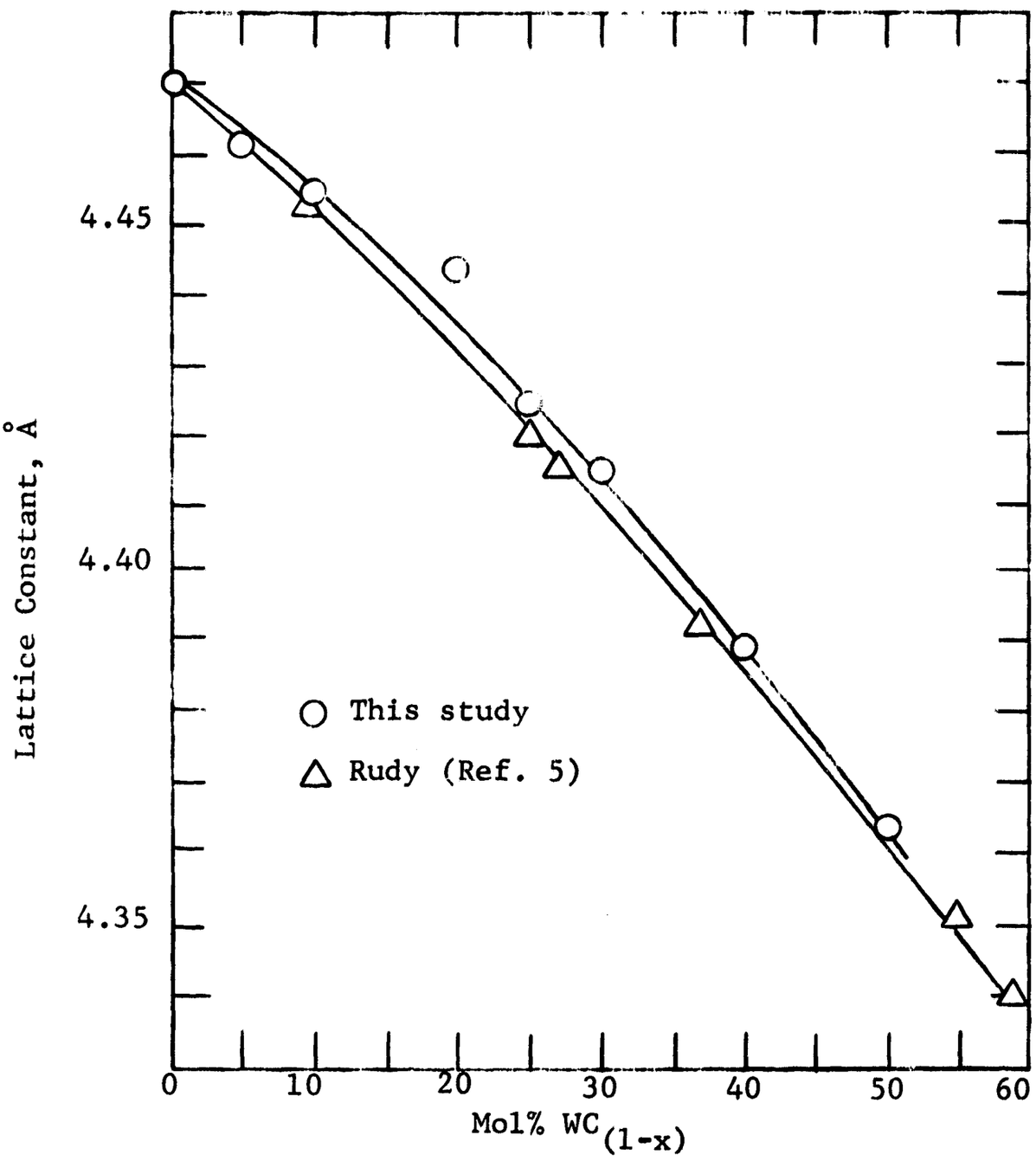


Fig. 5 LATTICE PARAMETERS OF NbC-$WC_{(1-x)}$ SOLID SOLUTIONS

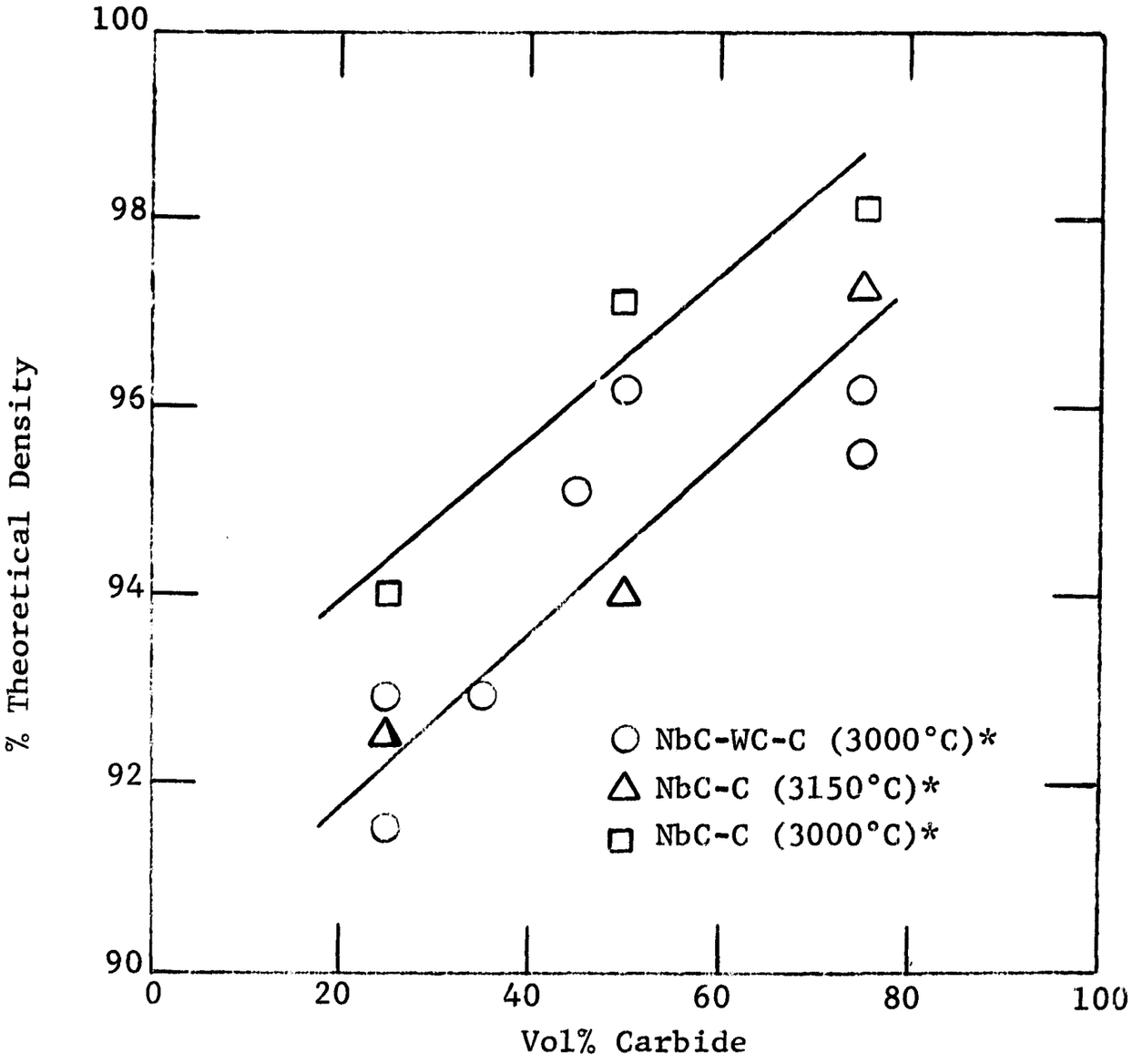


Fig. 6 % THEORETICAL DENSITY VS. CARBIDE CONTENT
(*HOT PRESSING TEMPERATURE)

order. Therefore, as the amount of carbide is increased in the composite, higher degrees of densification are achieved.

A comparison of data reveals that the NbC-WC-C and NbC-C(3150°C) values are in fairly good agreement as represented by the lower curve in Figure 6. The NbC-C (3000°C) composites achieved similar densities. However, it has been shown in previous work that although densification is achieved at 3000°C, a 3150°C hot pressing temperature is necessary to obtain the good diffusion and bonding for high temperature strength. This will be described further in the section on mechanical properties.

(b) Lattice Parameter Studies

Lattice parameter measurements have been used as a means of identification of the compositions of $NbC\text{-}WC_{(1-x)}$ solid solutions produced in the composites. As described in the previous section, experiments were conducted to determine lattice constant vs solid solution composition (Figure 5), and these data were used in our studies.

In most of the NbC-WC-C composites, reasonable agreement existed between the as-mixed and as-hot pressed solid solution compositions. There did appear to be a direct relationship, however, in loss of material vs amount of WC in the composition as shown in Figure 7. With increasing amounts of WC, more liquid phase would result during hot pressing leading to such loss of material.

For the materials which show greater losses of material, lattice parameter measurements as well as density values revealed a range in solid solution composition. As shown in Figure 8, a cone effect appeared to exist in these bodies, such that upper portions of the billet had lower carbide content and lesser amounts of $WC_{(1-x)}$ in solid solution. This is not unlike the phenomenon observed in NbC-C composites which were partially melted during fabrication,[7] and may be attributed to a greater pressure at the top plunger.

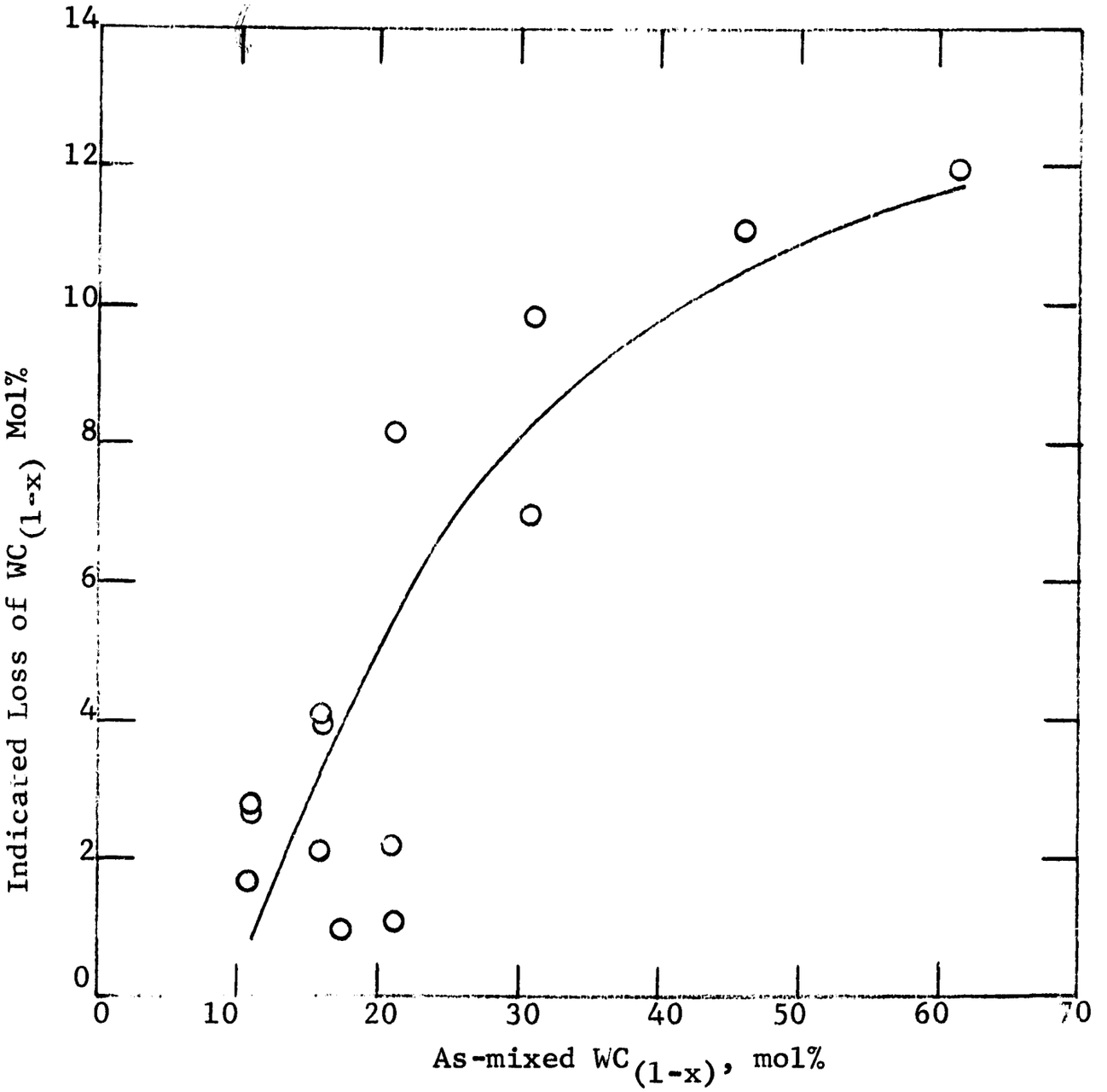
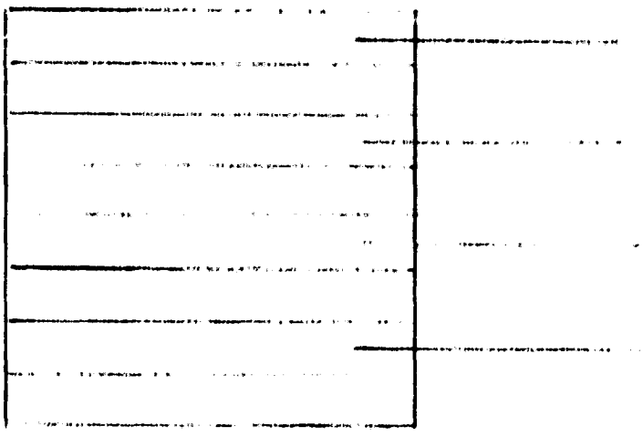


Fig. 7 LOSS OF WC AS A FUNCTION OF STARTING WC CONTENT



Density, g/cc	Mol% $WC_{(1-x)}$ in Solid Solution
5.06	—
5.14	13
5.26	—
5.43	17

Fig. 8 HETEROGENEITY OBSERVED IN COMPOSITE CONTAINING HIGH VOLUME RATIO OF WC (40NbC/10WC/50M3)

Although such bodies are heterogeneous, the high strengths obtained in these composites (see Mechanical Properties Section), are quite significant. Processing modifications to contain and restrict loss of material can probably produce the strongest composites possible.

(c) Microstructure

Representative microstructure of NbC-C appear in Figure 9 and those of NbC-WC-C are shown in Figure 10. There does not appear to be any radical differences with the addition of WC. In general, the M-3 graphite grains are still reasonably distinct, and there is little porosity. Perhaps the one significant difference is that the NbC-WC-C show less grain orientation than do the NbC-C composites.

(d) Microprobe Analysis

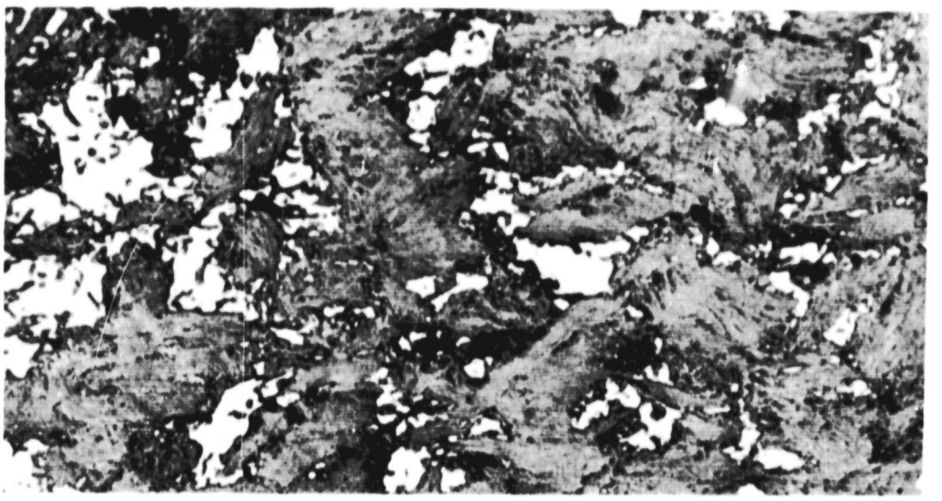
Examination of the 20NbC/5WC/75M-3 using the electron microprobe shows the presence of both Nb and W in the carbide phase (Figure 11). Solid solution formation is evident from this analysis; a fairly uniform dispersion of both elements is indicated. Due to the variation in detection and generation efficiencies of the various x-ray lines, no comparison can be made of element concentrations from photograph to photograph.

2. Mechanical Properties

Evaluation of mechanical behavior was concerned with both room and high temperature properties. Initial room temperature determination of flexural strength and elastic modulus provided rapid screening of the extent of bonding and also, an indication of uniformity through the billet. Elevated temperature evaluations included measurements of flexural strength and resistance to plastic deformation under flexural stress.

All room temperature data are based on an average of at least three test samples. High temperature data are averages of two or more measurements. The number of tests for any particular

50 μ



25NbC/75M-3

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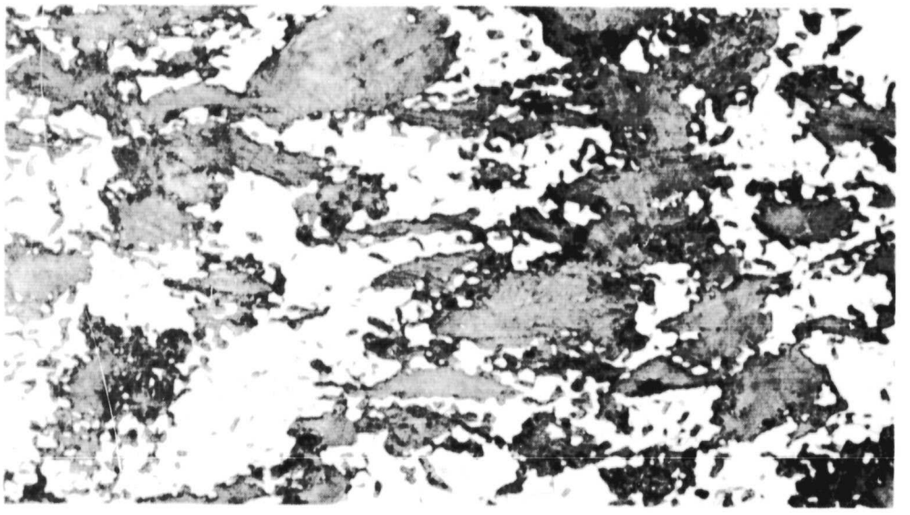

50NbC/50M-3

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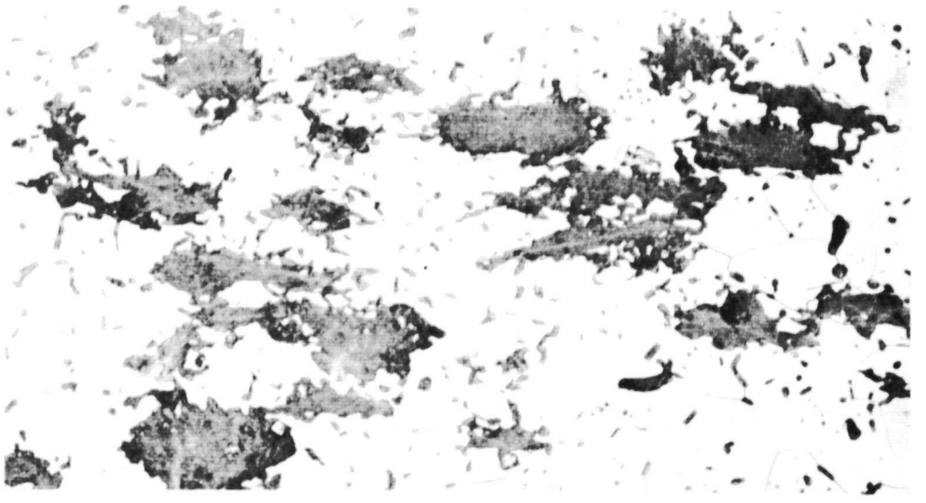


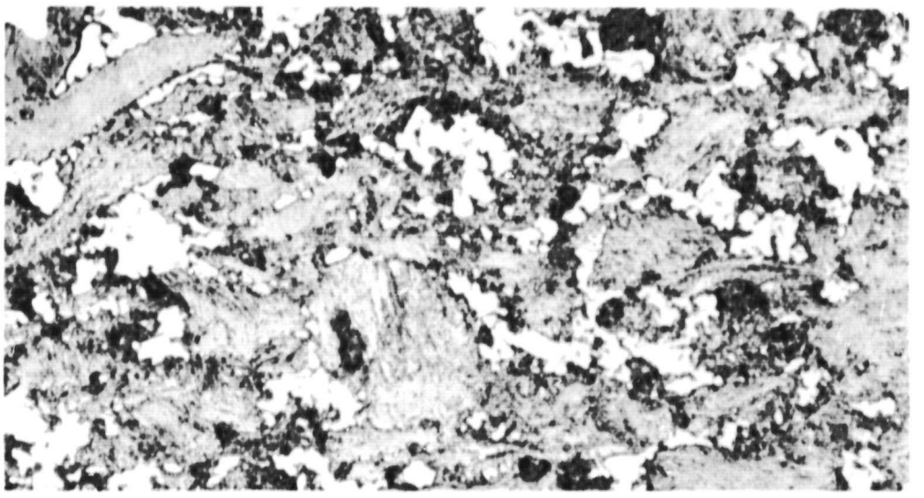
75NbC/25M-3

Neg. 36262

Mag. 200X
Etchant: $K_3Fe_2(CN)_6$-NaOH

Fig. 9 MICROSTRUCTURE OF NbC-C COMPOSITES

50 μ



20NbC/5WC/75M-3

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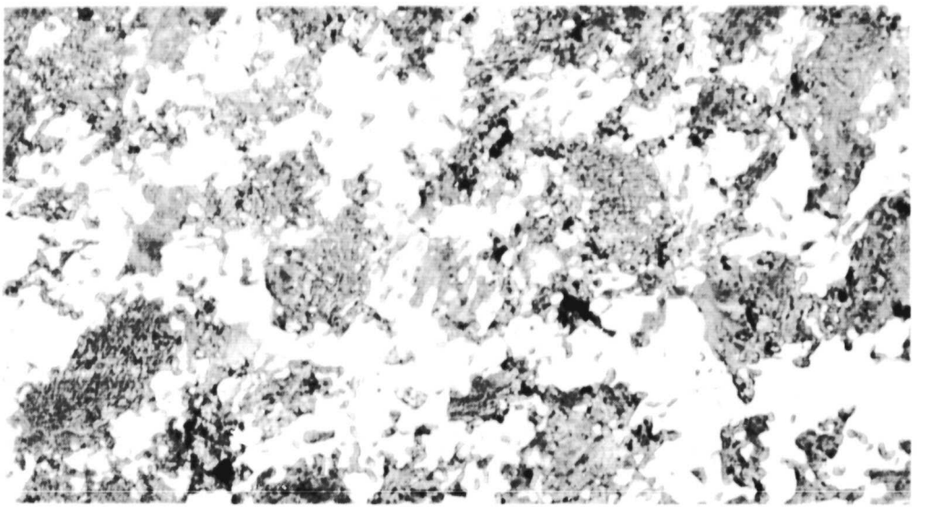
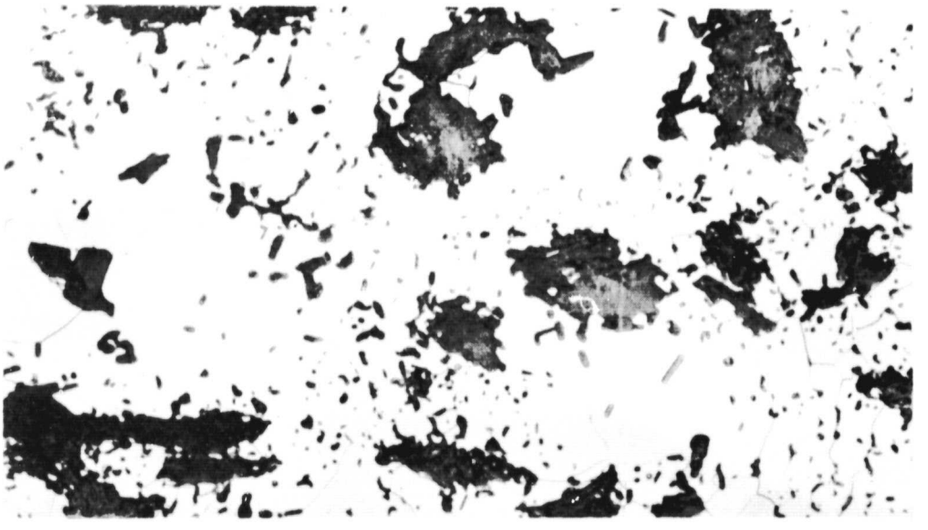


40NbC/10WC/50M-3

Neg. 36065

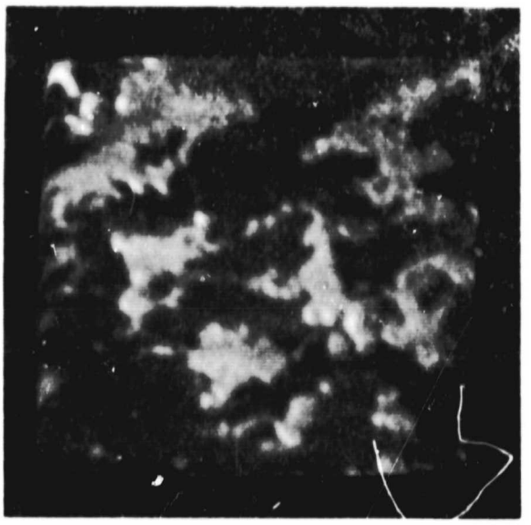


60NbC/15WC/25M-3

Neg. 36265

Mag. 200X
Etchant: $K_3Fe_2(CN)_6$-NaOH

Fig. 10 MICROSTRUCTURES OF NbC-WC-C COMPOSITES

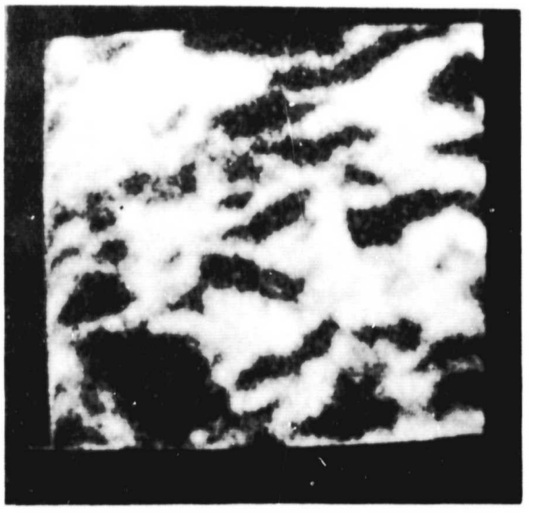


MP 1349

Electron Image

MP 1350

X-ray Image: W



MP 1351

X-ray Image: Nb

Mag. 150X

Fig. 11 ELECTRON MICROPROBE IMAGES SHOWING NbC-WC$_{(1-x)}$ SOLID SOLUTION(20NbC/5WC/75M-3)

property was limited in order to obtain the maximum amount of information about the various composites. In general, reproducibility of data was good; the coefficient of variation was less than 10% for any particular data point, unless otherwise specified.

(a) Flexural Strength

The room temperature strengths of both the NbC-C and NbC-WC-C composites as a function of carbide content are shown in Figure 12. Comparison of the NbC-C composites fabricated at the two temperatures, i.e., 3150°C and 3000°C, show that lower strengths exist for bodies hot pressed at 3000°C. This is probably due to the limited diffusion and bonding at the lower fabrication temperature.

The NbC-WC-C composites exhibited strengths comparable to those for NbC-C (3150°C). The linear plot for W/G strengths in Figure 12 represents the highest strengths observed for NbC-WC-C bodies. From these data we may speculate that:

1. The use of W as a fabrication aid in NbC-C composites fabricated at 3000°C results in bodies of higher room temperature strength.

2. NbC-WC-C composites hot pressed at 3000°C are as well-bonded as NbC-C composites fabricated at 3150°C.

Also included in Figure 12 is a curve for the W/G strengths of NbC-C composites incorporating calcined petroleum coke (CPC). These data are quite similar to the trend established in the present studies.

In Figure 13, flexural strengths at 2500°C vs carbide content are presented. Again a straight line plot may be used to indicate potential strengths for NbC-WC-C composites of varying carbide contents. These data show that at the low carbide level (25 vol%), additive composites exhibit strengths similar to those for the NbC-C standards. At higher carbide levels, there is a superiority in strength indicated for the additive composites,

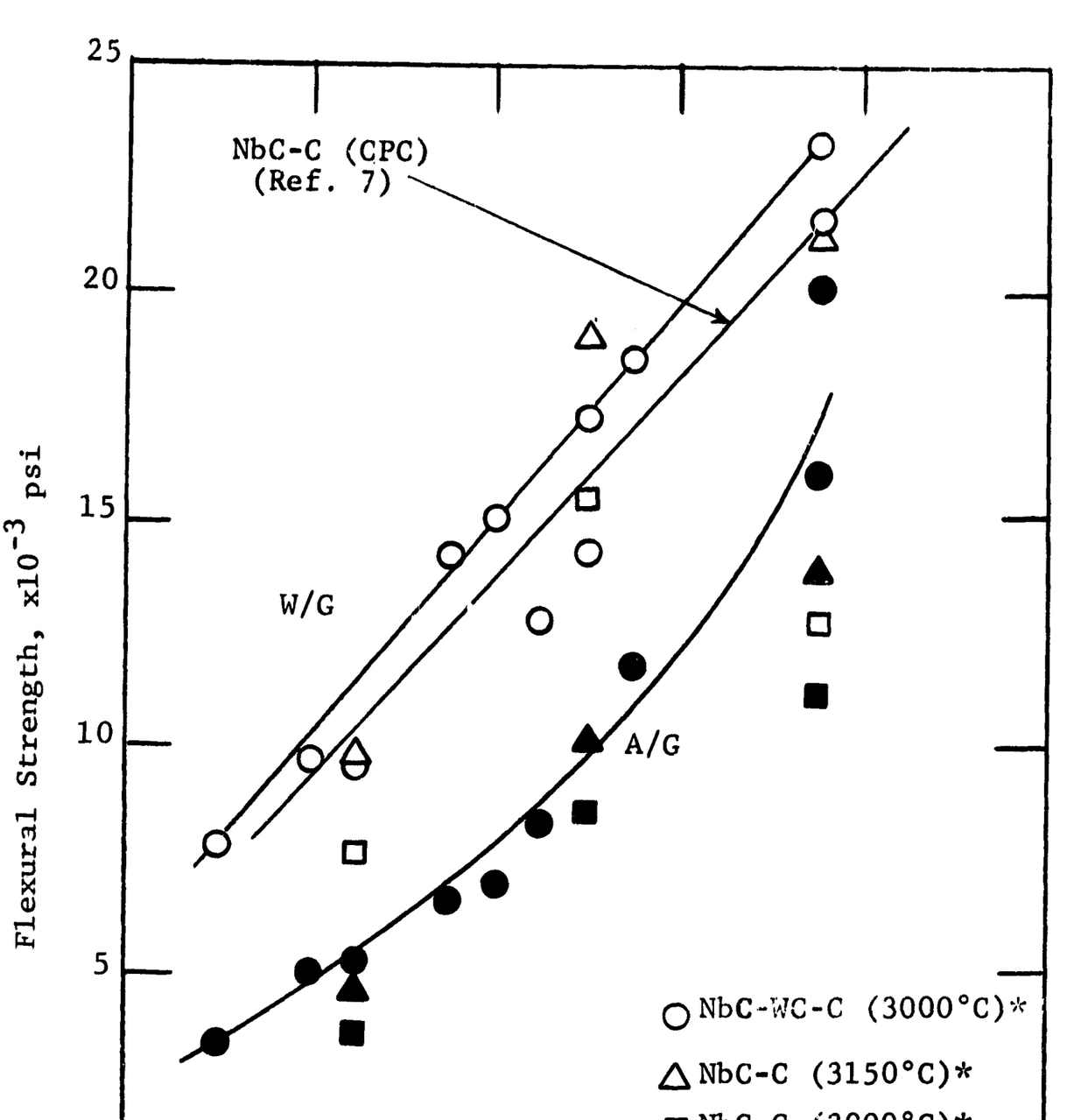


Fig. 12 ROOM TEMPERATURE FLEXURAL STRENGTHS OF NbC-WC-C COMPOSITES VS. CARBIDE CONTENT (*HOT PRESSING TEMPERATURE)

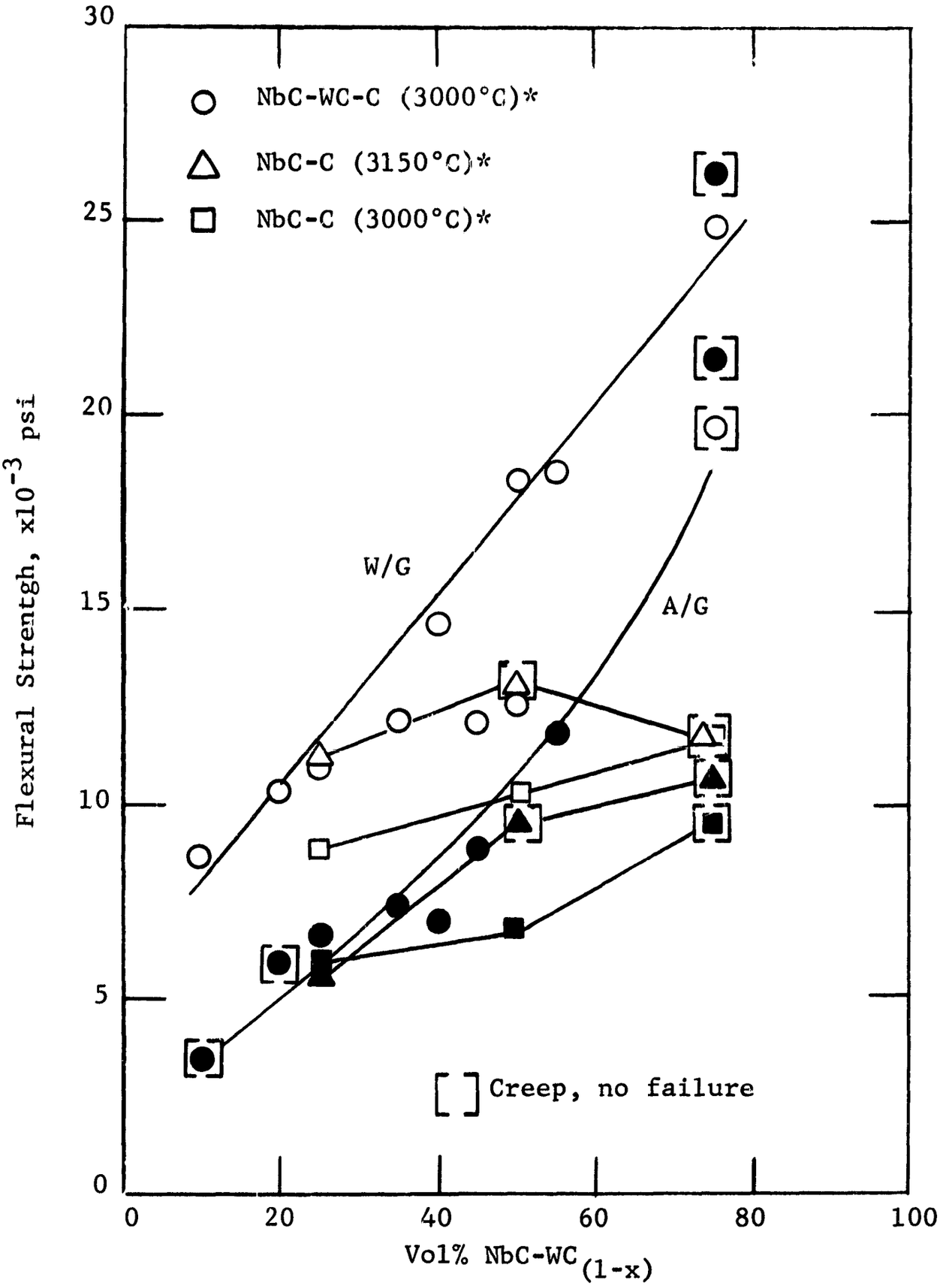


Fig. 13 2500°C FLEXURAL STRENGTHS OF NbC-WC-C COMPOSITES VS. CARBIDE CONTENT (*HOT PRESSING TEMPERATURE)

and this difference is quite pronounced at the 75 vol% carbide level. These data show clearly the advantages and benefits of using tungsten as a fabrication aid.

It would appear that of the two effects of using WC as an additive, i.e., graphitization aid and solid solution the latter has a more obvious effect. This can be observed in that superior strengths for the solid solution composites as compared to the standards, are shown at the higher carbide levels where the carbide phase would have a stronger contribution to properties. At the low carbide levels, increased strengths due to a graphitization effect of WC is not as evident. Perhaps the most significant point is that with the incorporation of WC, NbC-C composites of equivalent or superior properties to present state-of-the-art composites, can be produced at the lower fabrication temperature of 3000°C.

3. Thermal Expansion

Examination of high temperature behavior has included determinations of thermal expansion for the various composites. Coefficient of thermal expansion (CTE) values as a function of carbide content are shown in Figure 14. The trend toward isotropic behavior with increasing amounts of carbide is evident. At the 20 vol% carbide, the anisotropy ratio is about 2:1, while essentially non-directional behavior is observed for composites incorporating 75 vol% carbides.

These data also suggest that thermal expansion behavior is not significantly affected by incorporation of WC in NbC-C composites. The values for the 75 vol% carbide materials indicate that $NbC\text{-}WC_{(1-x)}$ solid solutions containing 10 to 20 mol% $WC_{(1-x)}$ have essentially the same expansion characteristics as NbC. The CTE value for NbC in this temperature range has been reported as $8.75\ in/in/°C \times 10^{-6}$.[6]

Previous work[7] had shown that NbC-C samples undergo permanent dimensional changes under thermal cycling. The present

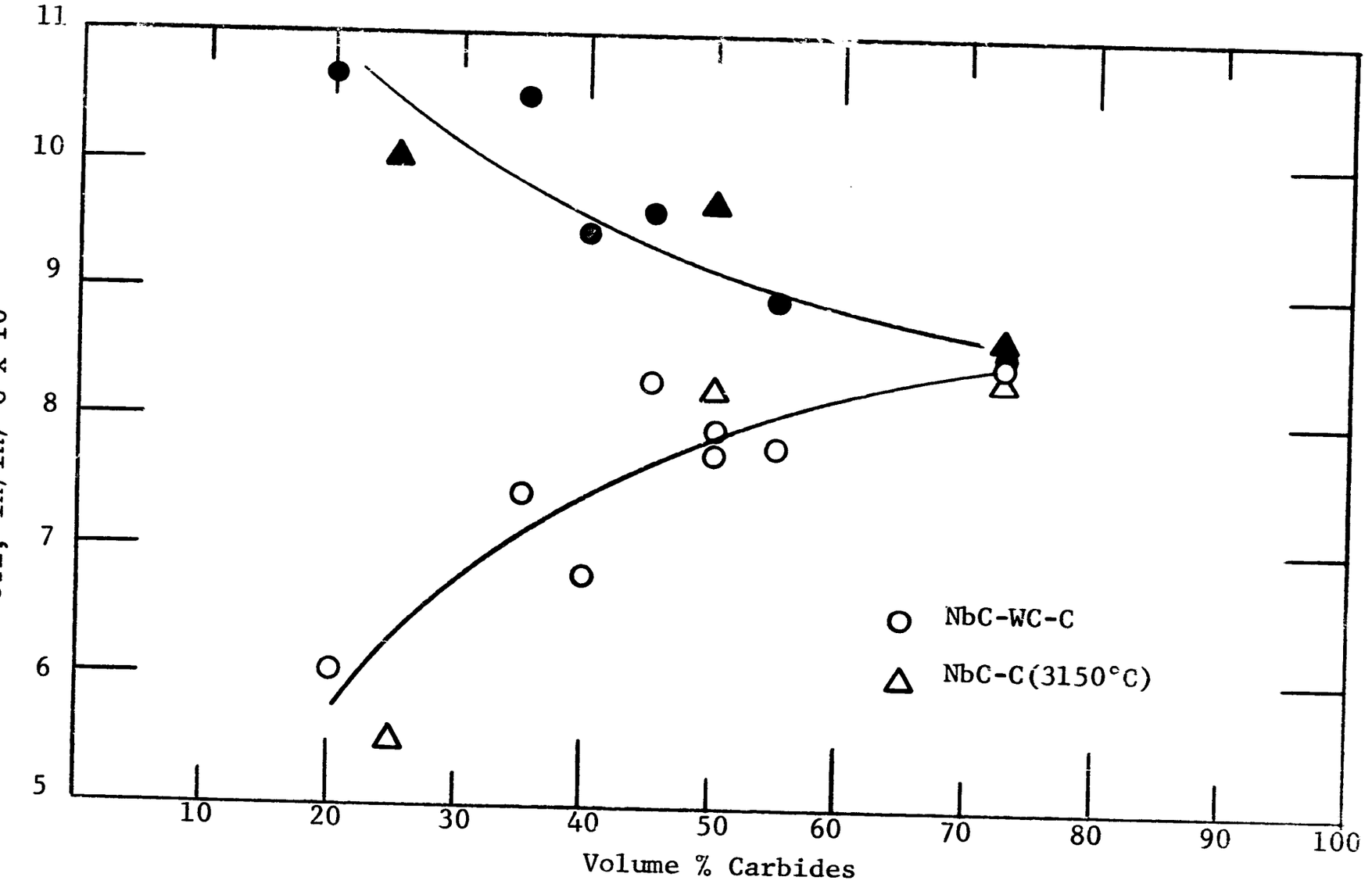


Fig. 14 THERMAL EXPANSION OF NbC-C AND NbC-WC-C COMPOSITES (ROOM TEMPERATURE TO 2500°C)

Fig. 14 THERMAL EXPANSION OF NbC-C AND NbC-WC-C COMPOSITES (ROOM TEMPERATURE TO 2500°C)

samples showed very little change. Extrapolation of second cycle curves back to room temperature confirmed this lack of change. It would appear that stresses were not imparted to these samples during fabrication, or were relieved by some undetermined mechanism. Such stress relaxation was thought to be the mechanism through which dimensional changes occurred in previous work.

C. TaC-WC-C System

In earlier work[7] with TaC-C composites containing less than 50 vol% carbide, temperatures in excess of 3250°C appeared necessary for obtaining dense, well-bonded composites. Even at this high hot-pressing temperature, graphite-rich TaC-C composites (20 to 50 vol% carbide), had somewhat lower strengths than comparable NbC-C composites. This is probably due to the limited carbide diffusion at about 3250°C which is still some 200°C below the TaC-C eutectic of 3450°C. Hot-pressing at temperatures closer to this solidus is hampered by rapid deterioration of the graphite mold at these temperatures.

A series of TaC-WC-C composites containing 20, 35, and 50 vol% carbide were fabricated at 3000°C. Although this is well below the 3250°C hot-pressing temperature used for TaC-C composites, it was anticipated that the graphitization effect with the use of WC would produce good bonding.

1. Physical Properties

(a) Density

Good densification was achieved for all of the bodies as shown by the data in Table II. The rather low value of 90.0% for 14TaC/6WC/80M-3 is somewhat misleading in that material loss during pressing occurred for this composite. This may be due to the formation (and loss), of greater amounts of a mobile liquid phase. As shown in Table II, this composite would have the most WC-rich solid solution (31.6 mol% WC), and a lower melting phase would exist until equilibrium was reached. The loss of carbide is reflected in the difference in WC content between the as-mixed

Table II

FABRICATION SUMMARY FOR TaC-WC-C COMPOSITES

Compositional Designation	Density, g/cc	% Theoretical Density	Lattice Constant Å	Mol% WC As Mixed	Mol% WC Hot Pressed
45TaC/5WC/50M-3	8.06	95.5	4.443	10.7	8
40TaC/10WC/50M-3	8.39	98.7	4.431	21.2	15
31.5TaC/3.5WC/65M-3	6.39	96.9	4.445	10.7	7
28TaC/7WC/65M-3	6.51	98.1	4.430	21.2	15
16TaC/4WC/80M-3	4.60	96.6	4.429	21.2	15
14TaC/6WC/80M-3	4.21	90.0	4.423	31.6	19

(31.6 mol%), and hot-pressed (19 mol%), as determined by x-ray analysis. Therefore, this particular composite probably had a total carbide content somewhat less than the pre-hot-pressed 20 vol% and would have a lower density.

(b) Microstructure

The microstructure of TaC-WC-C composites are shown in Figure 15. At the 20 vol% carbide level, clustering of carbide phase was evident, leaving fairly large patches of graphite phase containing little carbide (14TaC/6WC/80M-3). This lack of good dispersion is partially due to loss of material as described in the preceding section.

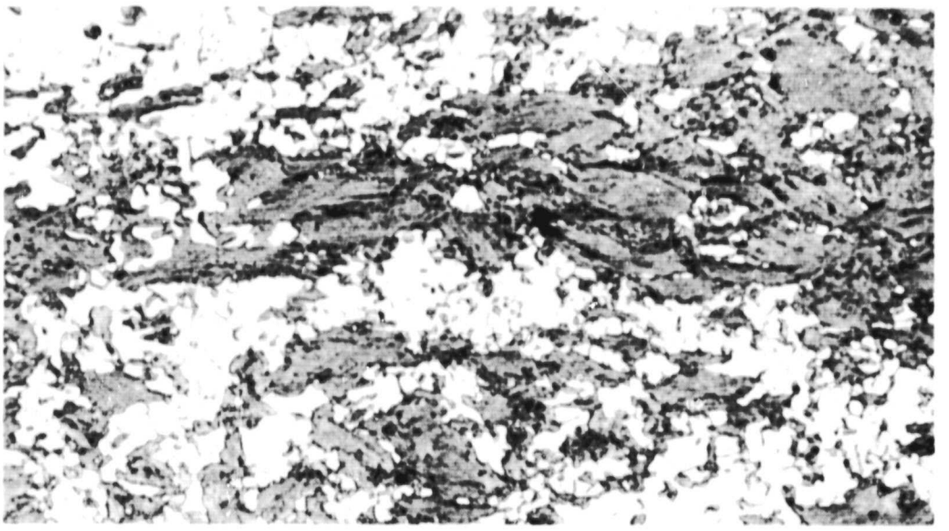
A more uniform structure was evident in higher carbides content (35 vol% and 50 vol%) composites. All of the TaC-WC-C microstructure were characterized by the fine grain size of the carbide phase, as determined by starting materials. The small particle size of the carbide also produced a fairly pronounced grain directionality.

2. Mechanical Properties

The properties of these composites are tabulated in Table III. The room temperature strengths are compared to those for the best TaC-C composites fabricated at 3250°C in an earlier program.[7] As shown in Figure 16, the data determined previously are represented by the solid lines, and the data points for the TaC-WC-C composites are plotted. The results show that the additive composites fabricated at 3000°C have strengths similar to those for non-additive composites hot-pressed at 3250°C, indicating that the WC was effective in promoting bonding at the lower (3000°C) fabrication temperature.

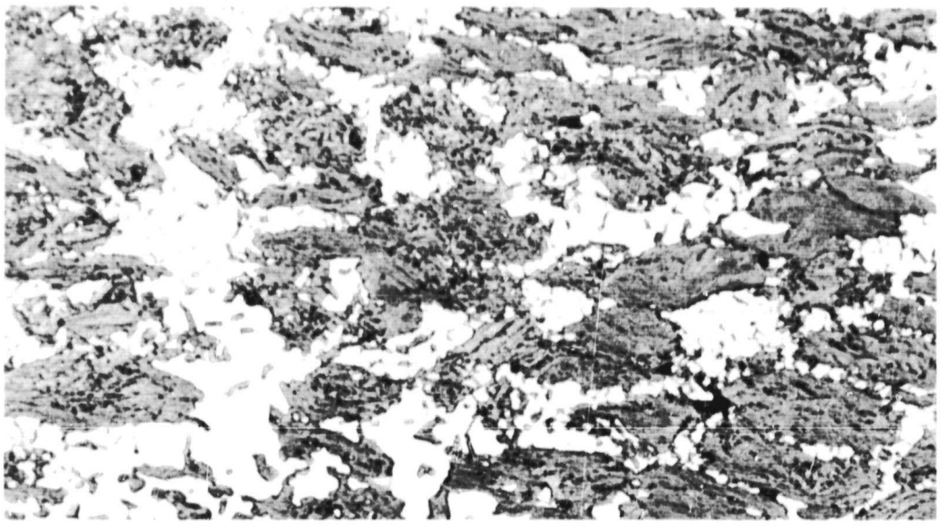
The flexural strengths at elevated temperatures as listed in Table III show that all composites exhibited good retention of strength. A plot of these data as a function of carbide content appears in Figure 17. Included in this graph is the

50μ



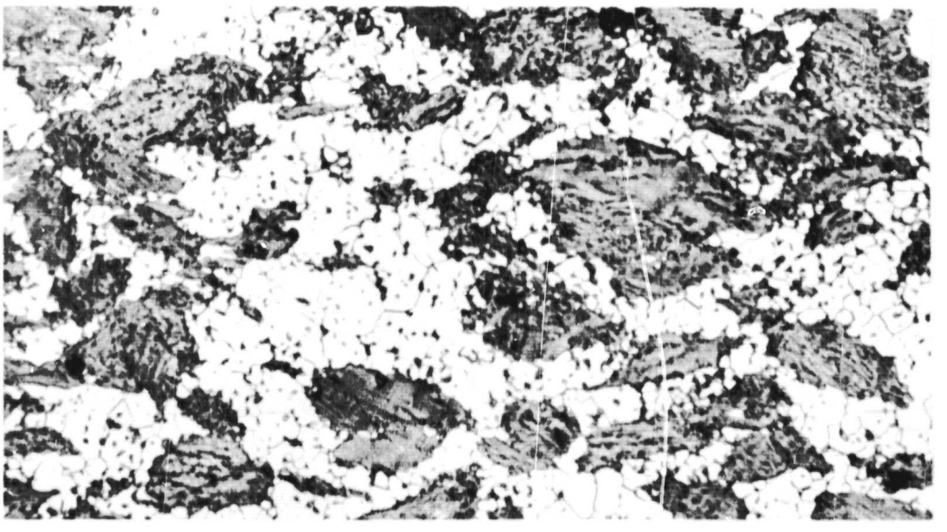
14TaC/6WC/80M-3

Neg. 37249



28TaC/7WC/65M-3

Neg. 37243



40TaC/10WC/50M-3

Neg. 37240 Mag. 200X
Etchant: $K_3Fe_2(CN)_6$-NaOH

Fig. 15 MICROSTRUCTURE OF TaC-WC-C COMPOSITES

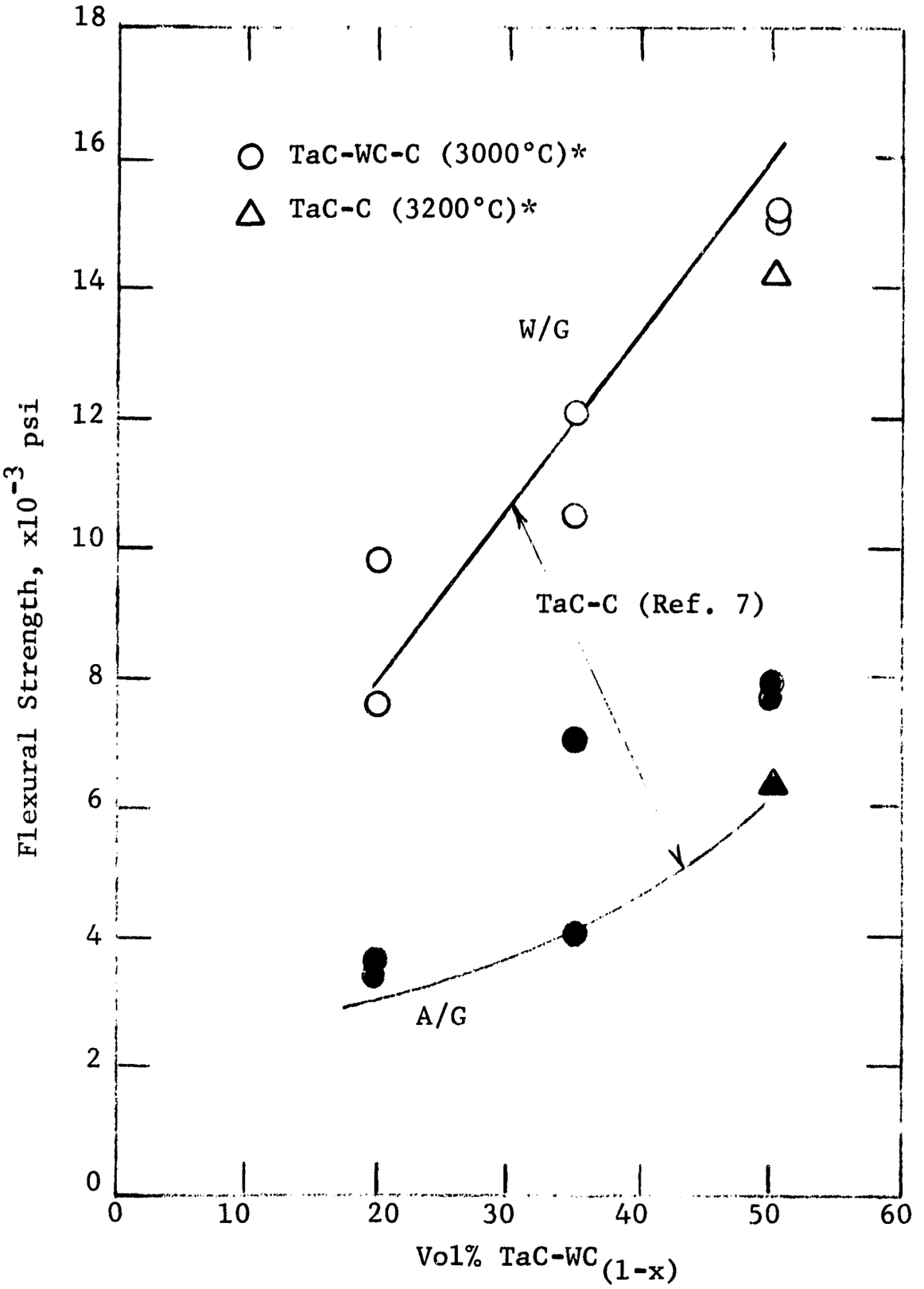


Fig. 16 ROOM TEMPERATURE FLEXURAL STRENGTHS OF TaC-WC-C COMPOSITES VS. CARBIDE CONTENT (*HOT PRESSING TEMPERATURE)

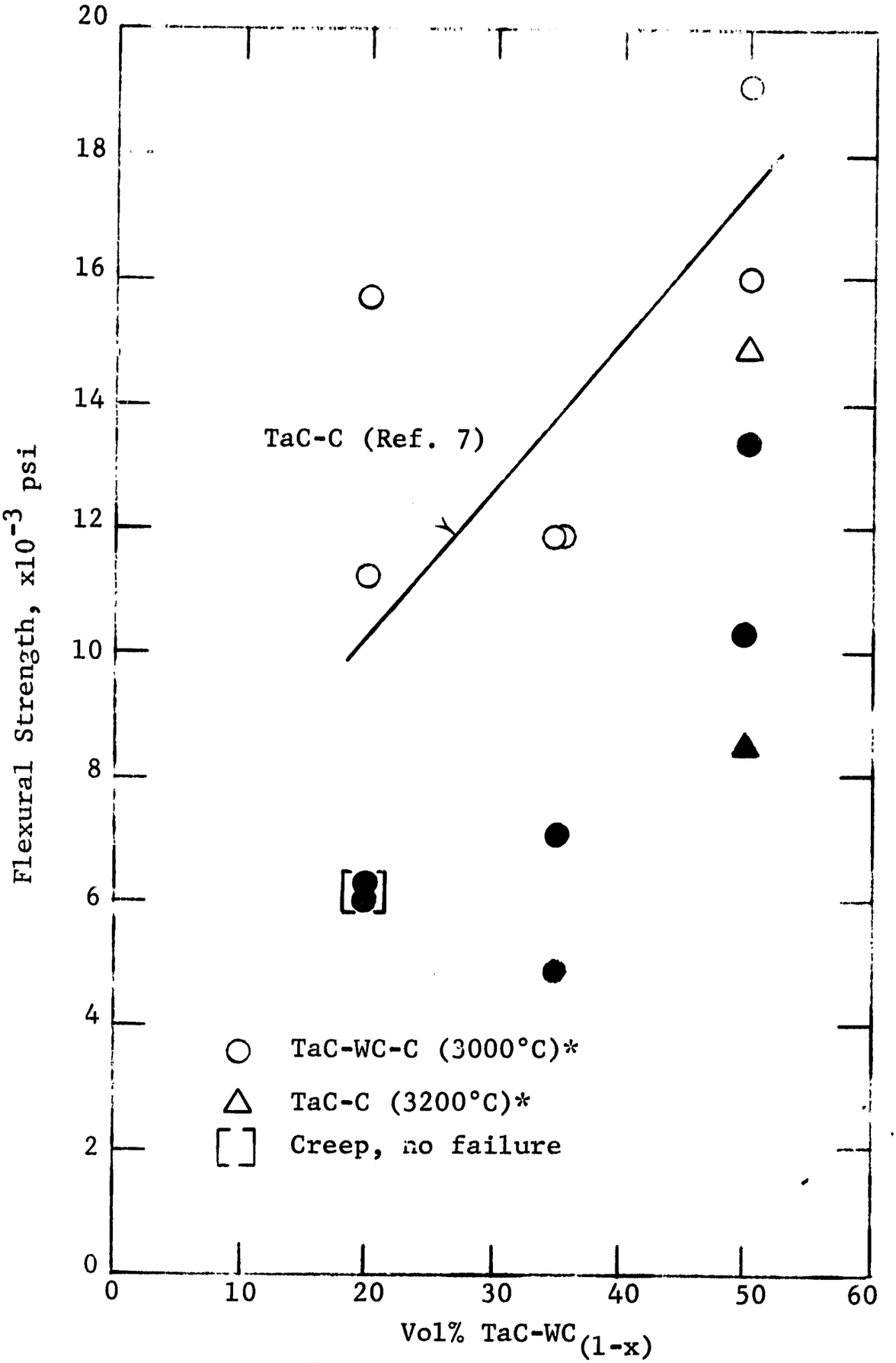


Fig. 17 2500°C FLEXURAL STRENGTHS OF TaC-WC-C COMPOSITES VS. CARBIDE CONTENT (*HOT PRESSING TEMPERATURE)

Table III

PROPERTIES SUMMARY FOR TaC-WC-C COMPOSITES

Compositional Designation	Grain Direction	Flexural Strength, psi RT	2000°C	2500°C	Elastic Modulus x10^6 psi	Electrical Conductivity, x10^4 mho-cm
45TaC/5WC/50M-3	W/G	15,180	18,510	19,110	11.5	1.23
	A/G	7,870	9,800	13,360	5.3	0.88
	A.R*	1.93	1.89	1.43	2.16	1.40
40TaC/10WC/50M-3	W/G	15,060	19,450	15,960	14.9	0.86
	A/G	7,750	11,400	10,280	6.4	0.57
	A.R.	1.94	1.71	1.55	2.33	1.51
31.5TaC/3.5WC/65M-3	W/G	12,140	14,410	11,890	6.6	0.76
	A/G	3,990	5,710	4,880	2.9	0.40
	A.R.	3.04	2.52	2.44	2.44	1.90
28TaC/7WC/65M-3	W/G	10,540	15,360	11,940	5.3	0.65
	A/G	7,040	8,100	7,060	3.7	0.38
	A.R.	1.50	1.90	1.69	1.41	1.71
16TaC/4WC/80M-3	W/G	7,640	13,240	11,180	3.0	0.48
	A/G	3,660	6,870	6,120**	1.5	0.22
	A.R.	2.09	1.93	1.83	1.97	2.18
14TaC/6WC/80M-3	W/G	9,820	16,140	15,700	3.3	0.70
	A/G	3,420	6,440	6,330**	0.7	0.23
	A.R.	2.87	2.51	2.48	4.53	3.04

*A.R. - Anisotropy ratio

**Highest stresses which could be applied before deformation rate exceeded load rate (crosshead speed = .04 in/min).

strength vs carbide content (solid line), determined for TaC-C composites.[2] As was the case at room temperature, the flexural strengths at 2500°C for TaC-WC-C composites fabricated at 3000°C compare favorably with those for TaC-C hot-pressed at 3250°C. In particular, the TaC-WC-C bodies incorporating 20 vol% carbides exhibited excellent strengths at 2500°C which were significantly higher than those at room temperature. In the W/G direction, the increase was about 50% and in the A/G direction, about 70%.

From these data, it would appear that the use of WC in TaC-C composites produces well-bonded composites at a hot-pressing temperature of 3000°C. This is of particular significance for composites with less than 30 vol% carbide; a comparison of 2500°C strengths between TaC-WC-C and NbC-WC-C bodies show that the TaC system is stronger (15,000 psi vs 10,000 psi).

D. NbC-B_4C-C System

1. Physical Properties

Two compositions were fabricated at 3000°C: 70NbC/5B_4C/25M-3 and 45NbC/5B_4C/50M-3. Theoretical densities were calculated using the assumption that the three phases in each composite remained discreet. These are compared with the measured densities:

	Density, g/cc	
Composition	Theoretical	Measured
70NbC/5B_4C/25M-3	6.15	6.11-6.21
45NbC/5B_4C/25M-3	4.77	4.64-4.79

It is highly unlikely that these materials attained 97-100% of theoretical density since this would mean that the graphite phase would be completely dense. Therefore, it appears probable that some reaction had occurred, forming a denser phase.

X-ray analysis showed the presence of NbC and C, both with undistorted lattices, and very faint traces of NbB_2. The theoretical density (x-ray) of NbB_2 is 7.161 g/cc which is less than that of NbC (7.798 g/cc). Since NbB_2 in a free state would

tend to lower the density of this material, it appears conceivable that it exists as an inclusion in the NbC lattice.

2. Mechanical Properties

Flexural strengths of these composites determined at room temperature, 2000°C, and 2500°C, are shown in Figure 18. For the 70NbC/5B_4C/25M-3, the values for the three samples at each test temperature were within 5%.

However, the 45NbC/5B_4C/50M-3 displayed a wide range; the values for this material are shown as individual points. There did appear to be some consistency based on the location in the billet, i.e., samples from the same row (longitudinal section) formed a grouping (Figure 19). Samples from Row E exhibited very high strengths (24,600 psi at room temperature and 23,000 psi at 2000°C), which were significantly higher than that observed for NbC-C or NbC-WC-C of equivalent carbide content. Row C, on the other hand, had very weak samples.

All samples displayed a drastic loss in strength at 2500°C. It may be that there is a low melting phase which seriously affects strength in this region. The reasons for the different anomalies in the boron system could not be determined within the scope of this program. It is hoped that this work might be continued at some future date.

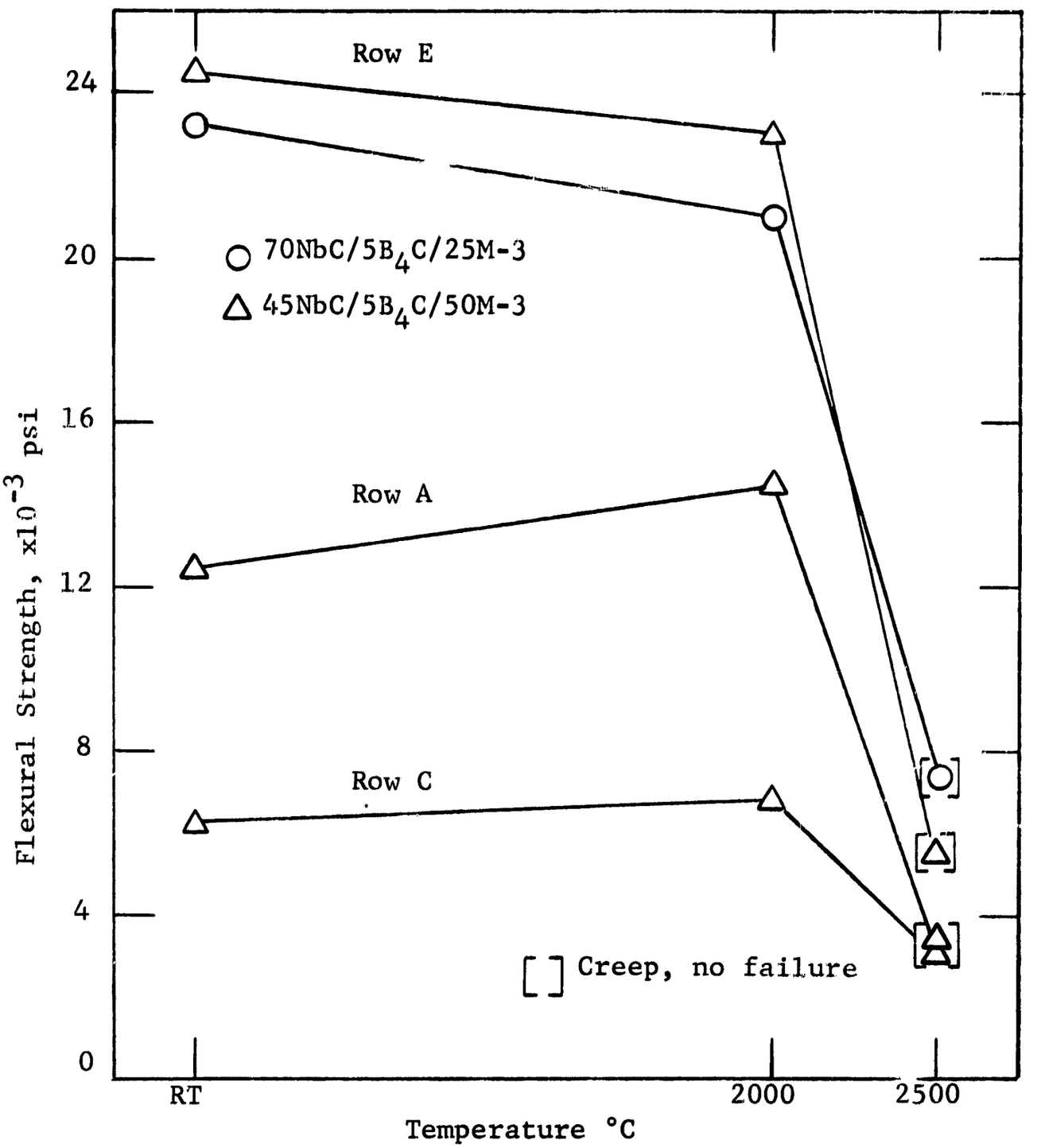


Fig. 18 FLEXURAL STRENGTH VS. TEMPERATURE FOR NbC-B_4C-C COMPOSITES

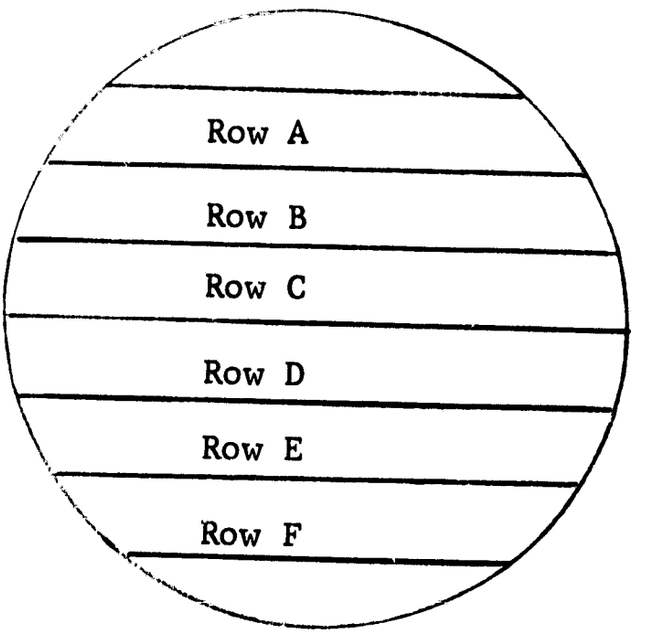


Fig. 19 SECTIONING SCHEME FOR NbC-B_4C-C COMPOSITES (TOP VIEW OF BILLET)

V. RECOMMENDATIONS FOR FUTURE WORK

Our studies with the use of tungsten as a fabrication aid in the NbC and TaC-C systems have shown that composites with excellent high temperature properties can be obtained at 3000°C. It is recommended that additional studies consider the following:

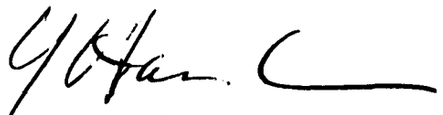
1. Fabrication - It may be possible to further lower the hot pressing temperature to as low as 2800°C and still obtain good high temperature materials. The pressure may be increased to 5000 psi to achieve good densification and bonding. The excellent properties exhibited by composites which have undergone considerable liquification suggest processing modifications. These may consist of changes in temperature and pressure as mentioned above, or incorporation of a liner which would limit material loss.

2. Materials - Analysis of phase diagrams suggest that the use of molybdenum as a fabrication aid can result in a greater amount of highly-ordered, reprecipitated graphite. The interesting results of the preliminary work with B_4C should be investigated further. This can produce high strength composites for use at intermediate temperatures up to 2000°C.

VI. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

The following personnel have contributed to this research program: S. A. Bortz, Y. Harada, E. Tan, J. L. Sievert, and E. T. Cannon. Data are contained in the following IITRI logbooks: C-19302, C-19404, C-19316, C-19329, C-19456, C-19467, C-19475, and C-19547.

Respectfully submitted,
IIT RESEARCH INSTITUTE



Y. Harada
Research Ceramist
Ceramics Research

APPROVED:

S. A. Bortz
Senior Engineer
Ceramics Research

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